Available online at www.sciencedirect.com
ScienceDirect
Materials Science and Engineering C 28 (2008) 188 – 194
MATERIALS SCIENCE & ENGINEERING C
www.elsevier.com/locate/msec

Enhanced oxidation of diclofenac sodium at a nano-structured electrochemical sensing film constructed by multi-wall carbon nanotubes–surfactant composite

Xiaofeng Yang [a,b], Fang Wang [a], Shengshui Hu [a,*]

[a] *Department of Chemistry, Wuhan University, Wuhan 430072, China*
[b] *Department of Pharmacy, Whenzhou Medical College, Wenzhou 325035, China*

Received 27 February 2006; received in revised form 16 November 2006; accepted 22 November 2006
Available online 4 January 2007

Abstract

A multi-walled carbon nanotubes (MWNTs)–dihexadecyl hydrogen phosphate (DHP) film-coated glassy carbon electrode (GCE) was fabricated, and the voltammetric determination method of diclofenac sodium was investigated on this modified electrode by using different kinds of electrochemical techniques. The results showed that this nano-structured film electrode exhibits excellent enhancement effects on the electrochemical oxidation of diclofenac sodium. The oxidation peak current of diclofenac sodium at this film-modified electrode increased significantly compared with that at a bare glassy carbon electrode. Based on the experiment outcomes a possible mechanism was proposed and discussed. The proposed method was demonstrated by using diclofenac sodium tablets and the result was satisfying.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Diclofenac sodium; Multi-walled carbon nanotubes (MWNTs); Nanoparticles; Voltammetric determination

1. Introduction

In the last decades, nanoparticle research has witnessed tremendous interest in nanoscience and nanotechnology. As a kind of nonmetal particle, carbon nanotubes (CNTs) have become promising candidates of intense researches because of their structural, mechanical and electronic properties in a wide range of applications. The publication of numerous works shows the significance of CNTs in electrochemistry and electroanalytical chemistry. Recent studies demonstrated that CNT can enhance the electrochemical reactivity of important biomolecules [1,2], and can promote the electron-transfer reactions of proteins (including those where the redox center is embedded deep within the glycoprotein shell) [3,4]. In addition to enhanced electrochemical reactivity, CNT-modified electrodes have been shown useful to accumulate important biomolecules (e.g., nucleic acids) [5] and to alleviate surface fouling effects (such as those involved in the NADH oxidation process) [2]. The remarkable sensitivity of CNT conductivity to the surface adsorbates permits the use of CNT as highly sensitive nanoscale sensors [6–13].

Diclofenac sodium (DFNa) (sodium [*o*-(2, 6-dichloroanilino) phenyl] acetate) shown in Fig. 1 is a well-known representative of non-steroidal anti-inflammatory drugs (NSAIDs) with strong anti-pyretic, analgesic and anti-inflammatory properties [14]. It is widely used in clinical medicine for the treatment of inflammatory conditions such as rheumatoid arthritis, osteoarthritis and ankylosing spondylitis [15,16]. To date, many means have been employed for the determination of diclofenac sodium, such as capillary zone electrophoresis (CZE) [17], high performance liquid chromatography (HPLC) [18], high-performance liquid chromatography-mass spectrometry (HPLC-MS) [19], spectrophotometric [20], spectrofluorometric [21], thin-layer chromatography [22,23], gas chromatography [24,25], and polarographic analysis [26]. To the best of our knowledge, very little has been reported on voltammetric determination of diclofenac sodium, because the electrooxidation of diclofenac sodium proceeded very slowly and almost no current response was observed at the usual electrode. In this work, a multi-walled

---

* Corresponding author. Tel.: +86 27 8721 8904; fax: +86 27 6875 4067.
E-mail address: sshu@whu.edu.cn (S. Hu).

0928-4931/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2006.11.006

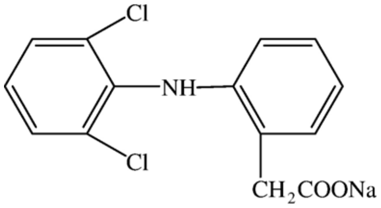

Fig. 1. Chemical structure of diclofenac sodium.

carbon nanotubes (MWNTs)–dihexadecyl hydrogen phosphate (DHP) film coated glassy carbon electrode (GCE) for the determination of diclofenac sodium was structured. MWNTs consist of several layers of cylindrical graphitic sheets with nanometer diameter, which are one of distinct types of carbon nanotubes (CNTs) structures. The enhanced electrooxidation and voltammetry of diclofenac sodium at the surface of MWNTs-DHP film coated GCE in sodium acetate–acetic acid buffer solution (pH 5.0) was attributed to the unique properties of MWNTs such as large specific surface area and strong adsorptive properties providing more reaction sites. The proposed method was successfully applied to determine diclofenac sodium in diclofenac sodium enteric-coated tablets.

2. Experimental

2.1. Apparatus and reagents

Dihexadecyl hydrogen phosphate (DHP) was gotten from Fluka Chemical Reagent Corporation and stored at −18 °C. MWNTs (obtained from the Institute of Nanometer Materials, Central China Normal University, China) were synthesized by a catalytic pyrolysis method and then refluxed slightly in HNO_3 for 48 h (95 °C) in order to get purified and oxidized MWNTs. Nitric acid purified MWNTs containing large numbers of carboxyl or other oxygenic groups at their terminus are easily dispersed. Diclofenac sodium (DFNa) was purchased from the National Institute for the Control of Pharmaceutical and Biological Products, China. After the torrefaction at 105 °C for 3 h diclofenac sodium (DFNa) was dissolved in doubly distilled water to form a stock solution at a concentration of 1.0×10^{-2} mol/L. The sample solution was prepared by dissolving 25 mg diclofenac sodium enteric-coated tablets in 250 mL doubly distilled water and separated via centrifugal effect. The supernatant fractions were collected for determination. Other chemicals used were analytical reagents. All the chemicals were used without further purification and all the solutions were prepared with doubly distilled water.

All the electrochemical measurements were performed on a CHI 830 electrochemical analyzer (Shanghai Chenhua Co., China) in a three-electrode system. The working electrode was a MWNTs film coated glassy carbon electrode (GCE). A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Ultraviolet (UV)–visible absorption spectroscopy was recorded on a UV-7502PC spectrophotometer (Shanghai Xinmao Instrument Co. Ltd., China).

2.2. Preparation of the MWNTs–DHP film coated GCE

5 mg nitric acid-treated MWNTs and 5 mg DHP were dispersed together in 5 mL redistilled water to give a 1 mg/mL black MWNTs–DHP suspension with the aid of ultrasonic agitation for about 40 min. Prior to modification, the GCE (A=0.072 cm^2) was mechanically polished with a polishing microcloth containing 0.05 μm Al_2O_3 slurry to a mirror finish, and then carefully cleaned in 1:1 HNO_3–H_2O (v/v) and ethanol (C_2H_5OH), water in turn via ultra-sonication each for 2 min, and finally allowed to be aired. Finally, 10 μL of the MWNTs–DHP suspension was cast on the GCE surface and air dried. Then a stable and uniform MWNTs–DHP film was formed. In the same way, acetylene black (AB)–DHP film coated GCE and DHP film without MWNTs coated GCE was obtained.

2.3. Experiment in details

A certain volume of 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) was used as the supporting electrolyte in a conventional electrochemical cell. At the beginning of experiment, MWNTs–DHP film coated GCE was scanned by successive cyclic voltammetric sweeps between 0.40 V and 1.10 V at 100 mV/s to get a steady cyclic voltammograms. Then 50 μL of 1.0×10^{-2} mol/L diclofenac sodium stock solutions was placed into the cell to make up 10 mL mixture solution. The accumulation was carried out at open circuit via stirring the solution for 4 min, and then kept quiet for 8 s. The voltammograms were recorded using a cyclic potential scan between 0.40 V and 1.10 V. After each measurement the modified electrode was refreshed by successive cyclic voltammetric sweeps in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) (between 0.0 V and 1.0 V at 100 mV/s) to get a reproducible electrode surface.

3. Results and discussion

3.1. The enhanced voltammetric behaviors of diclofenac sodium at MWNTs–DHP sensing film

The electrochemical oxidation of 5.0×10^{-5} mol/L diclofenac sodium at the MWNTs–DHP film coated GCE in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) were examined by cycle voltammetry (CV) between 0.40 V and 1.10 V. The cyclic voltammograms are illustrated in Fig. 2. A well-defined oxidation peak is observed at about 0.69 V when potential sweeps from 0.40 V to 1.10 V in the first cyclic sweep. It may be due to oxidation or disassembly of aniline group in diclofenac molecules. However, no peak appears on the reversal sweep, indicating that the electrochemical behaviors of diclofenac sodium at the MWNTs–DHP film coated GCE are a totally irreversible process. During following successive cyclic sweeps, the electrochemical responses of diclofenac sodium become very poor, resulting from the fact that the electrode surface is blocked by the strong adsorption of the reaction products which reduces the effective reaction sites at the modified electrode surface.

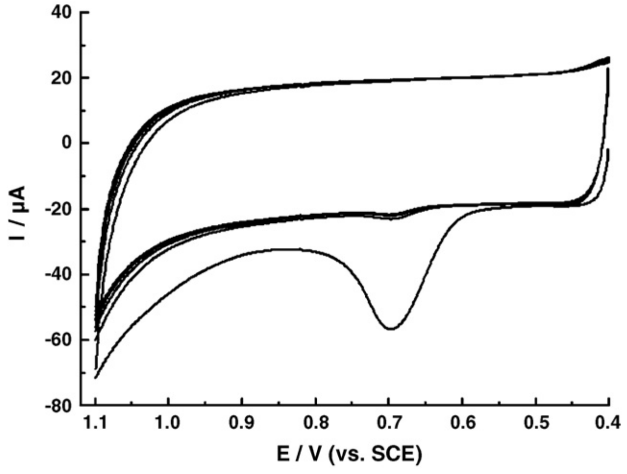

Fig. 2. Successive cyclic voltammograms of 5.0 × 10$^{−5}$ mol/L diclofenac sodium in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) at MWNTs–DHP film-coated GCE. Scan rate, 100 mV/s.

In order to illuminate the enhancement properties of MWNTs–DHP film at the GCE for the oxidation of diclofenac sodium, the linear sweep voltammetric responses of 5.0× 10$^{−5}$ mol/L diclofenac sodium are tested at different working electrodes including DHP film modified GCE (curve a in Fig. 3), bare GCE (curve b in Fig. 3), acetylene black (AB)–DHP film coated GCE (curve c in Fig. 3) and MWNTs–DHP film coated GCE (curve d in Fig. 3). The peak current of diclofenac sodium greatly increases at MWNTs–DHP film coated GCE (curve d in Fig. 3). It is believed that MWNTs show highly effective enhancement to diclofenac sodium oxidation because of its large specific surface area and subtle electrical properties, which provides enough effective reaction sites to increase the electron exchange rate. On the contrary, under the same experiment conditions and the peak current of diclofenac sodium almost disappear at DHP film modified GCE (curve a in Fig. 3) because the DHP film blocks the mass transport and electron transfer of diclofenac sodium. Similar results are obtained at bare GCE (curve b in Fig. 3). Compared to that at MWNTs–DHP film coated GCE (curve c in Fig. 3) the oxidation peak potential of diclofenac sodium shifts negatively at acetylene black (AB)–DHP film coated GCE, but the peak current is smaller than that.

3.2. Effects of the amount of MWNTs on oxidation diclofenac sodium

On the basis of above discussions, MWNTs can enhance the current responses of diclofenac sodium at the MWNTs–DHP film-coated GCE. So the amount of MWNTs can affect the oxidation current of diclofenac sodium in the nature of things. And then the relationship between the oxidation peak current and the film thickness determined by the amount of MWNTs–DHP dispersion on the GCE surface was estimated. The result was list in Fig. 4. In general, the oxidation peak current of diclofenac sodium increased quickly with the increase of the amount of MWNTs–DHP dispersion cast on the GCE surface in the range of volume from 0 to 8 µL. Further improving the amount of MWNTs–DHP dispersion, the peak current remained stable. As a result, 10 µL of 1 mg/mL MWNTs–DHP suspension was suitable for the structure of MWNTs–DHP film electrode.

3.3. Influences of supporting electrolyte on enhancement effects of MWNTs

The conditions of the electrolyte, such as types of electrolyte, are a key factor that affects the electrochemical properties of MWNTs and state of target molecules, as well as the sensitivity of voltammetric determination of diclofenac sodium. The electrochemical responses of 5.0 × 10$^{−5}$ mol/L diclofenac sodium at MWNTs–DHP film electrode in different supporting

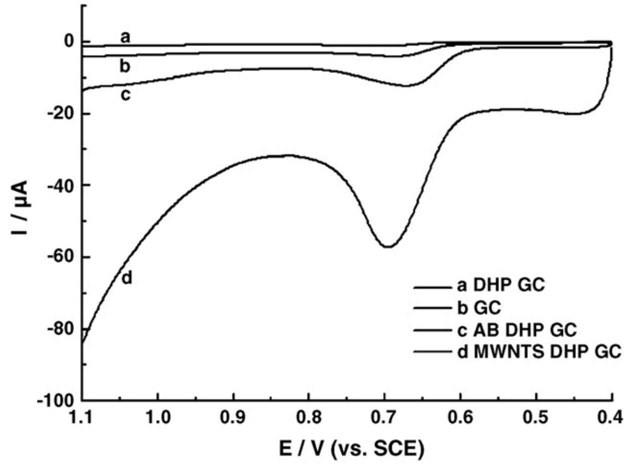

Fig. 3. Linear sweep voltammetric responses of 5.0 × 10$^{−5}$ mol/L diclofenac sodium in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) at DHP film modified GCE (a), bare GCE (b), acetylene black (AB)–DHP film coated GCE (c) and MWNTs–DHP film coated GCE (d). Scan rate, 100 mV/s.

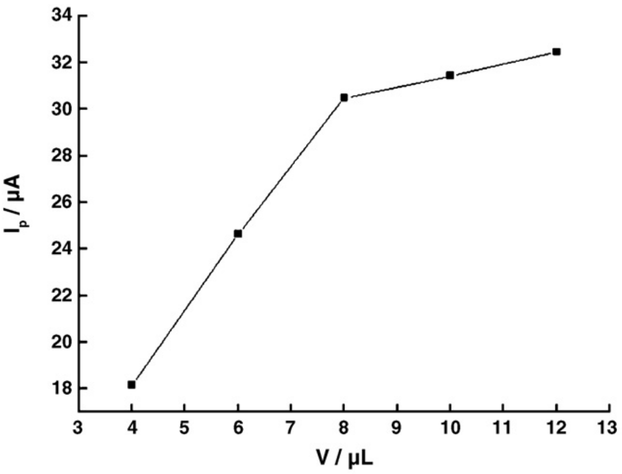

Fig. 4. Dependence of the peak current of 5.0 × 10$^{−5}$ mol/L diclofenac sodium on the amount of MWNTs–DHP dispersion on the GCE surface in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0).

Table 1
Influences of different buffer solution on the oxidation of 5.0×10^{-5} mol/L diclofenac sodium ($n \geq 10$)

PBS, pH	8.06	7.02	6.00	5.09	4.07	3.05	2.08
I_p (μA)	–	5.59	11.72	17.54	25.85	34.48	40.09
NaAc–HAc, pH			6.22	5.3	5.0	4.1	
I_p (μA)			11.50	20.20	27.18	32.25	
Sodium citrate–HCl, pH					4.02		2.05
I_p (μA)					17.78		27.56
Sodium citrate–NaOH, pH		6.69					
I_p (μA)		–					
Sodium tartrate–tartaric acid, pH				4.2	3.8	3.0	2.0
I_p (μA)				25.95	29.34	34.43	40.03
Borax–HCl, pH	8.13	7.6					
I_p (μA)	–	4.06					
Borax–NaOH, pH	9.94						
I_p (μA)	–						

Accumulation time is 60 s.
Scan rate: 100 mV/s.

electrolytes were tested by cycle voltammetry (CV), including 0.1 mol/L phosphate buffer solution (PBS, pH 4.5–8.0), sodium acetate–acetic acid buffer solution (NaAc–HAc, pH 3.5–5.6), sodium citrate–hydrochloric acid (HCl) buffer solution (pH 1.0–4.0), sodium citrate–sodium hydroxide (NaOH) buffer solution (pH 5.0–7.0), sodium tartrate–tartaric acid buffer solution (pH 1.4–4.5), borax–hydrochloric acid buffer solution (pH 7.6–9.2), borax–sodium hydroxide buffer solution (pH 9.2–12.3) and other different acids and alkalis or neutral solution including $HClO_4$ (0.1 mol/L), H_2SO_4 (0.05 mol/L), HCl (0.1 mol/L), HAc (0.1 mol/L), KCl (0.1 mol/L) and NaOH (0.1 mol/L); the corresponding data were listed in Tables 1 and 2, respectively. As shown in the two tables, the values of oxidation peak currents increased greatly with the increase of solution pH or the ionization of acid. And then there was no electrochemical response of diclofenac sodium in alkaline aqueous lacking the presence of enough protons. In the same way, the value of peak current obtained in KCl was not satisfying. It is found that the peak current became the highest in 0.1 mol/L $HClO_4$ and the voltammogram shape was well defined, but the stability of modified electrode was not good owing to the strong oxidation ability of $HClO_4$. In other strong acid electrolytes, bad stability could be found too. When the buffer solution pH is smaller than 5.0, the determination results become unsteady. Although the oxidation of diclofenac sodium involved proton transfer, too many protons would not benefit the electrode process. Considering the data in Tables 1 and 2, sodium acetate–acetic acid buffer solution (pH 5.0) is the most suitable electrolyte for the electrochemical detection of diclofenac sodium.

Table 2
Effects of different acids and alkalis or neutral salt solution on the oxidation of 5.0×10^{-5} mol/L diclofenac sodium ($n \geq 10$)

$HClO_4$ (0.1 mol/L)	H_2SO_4 (0.5 mol/L)	HCl (0.1 mol/L)	HAc (0.1 mol/L)	KCl (0.1 mol/L)	NaOH (0.1 mol/L)
70.65	28.92	52.49	16.41	4.09	–

Accumulation time is 60 s. Scan rate: 100 mV/s.

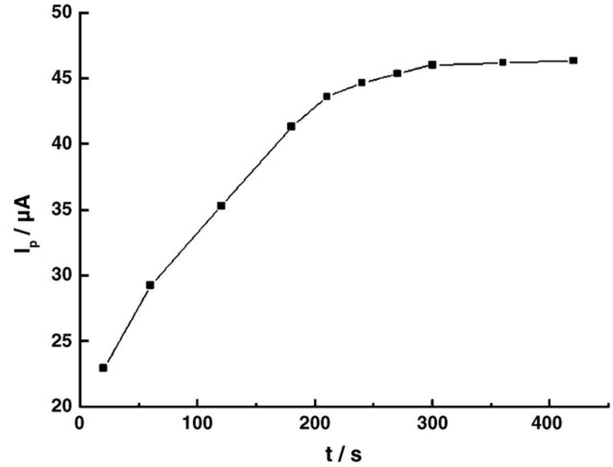

Fig. 5. Influences of accumulation time on the peak current of 5.0×10^{-5} mol/L diclofenac sodium at MWNTs–DHP film-coated GCE in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0).

3.4. Adsorption properties of MWNTs

3.4.1. Influences of accumulation potential and time

The accumulation time significantly affects the oxidation peak current of 5.0×10^{-5} mol/L diclofenac sodium as shown in Fig. 5 through changing its surface concentration on MWNTs–DHP composite film electrode. The oxidation peak current is enhanced greatly with the increase of the accumulation time within the first 4 min and then it remained almost unchanged. It may be contributed to the saturated adsorption of diclofenac sodium on the MWNTs–DHP film-coated GCE surface. It is the adsorption accumulation that affects the oxidation peak current of diclofenac sodium. It comes to the conclusion that large specific surface area and unique structure of MWNTs bring on the great accumulation efficiency. The accumulation potential is also a major factor which affects the voltammetric response in comparison with the other accumulation condition, the open circuit potential. The effect of the accumulation potential on the peak current was evaluated. The oxidation peak current of 5.0×10^{-5} mol/L diclofenac sodium has greatly changed as the accumulation potential shifted from 0.40 V to −0.40 V (Fig. 6), suggesting that the accumulation potential has an apparent influence on the oxidation process of diclofenac sodium at the MWNTs–DHP film-coated GCE. The oxidation peak current gets to the maximum value at 0.00 V; moreover, this value is close to that obtained at open circuit. Maybe the negative and positive accumulation potentials would endow the modified electrode surface with different electric characteristics such as the net electric charge of the surface. The electric charge condition of the modified electrode surface would directly influence the adsorption and oxidation reaction of diclofenac sodium involving electron and proton transfer. So considering the value of oxidation peak current and the convenience of experimental operation an open circuit accumulation was optimal condition.

3.4.2. Chronocoulometry

The method of chronocoulometry was used to characterize the oxidation of 4.0×10^{-4} mol/L diclofenac sodium at

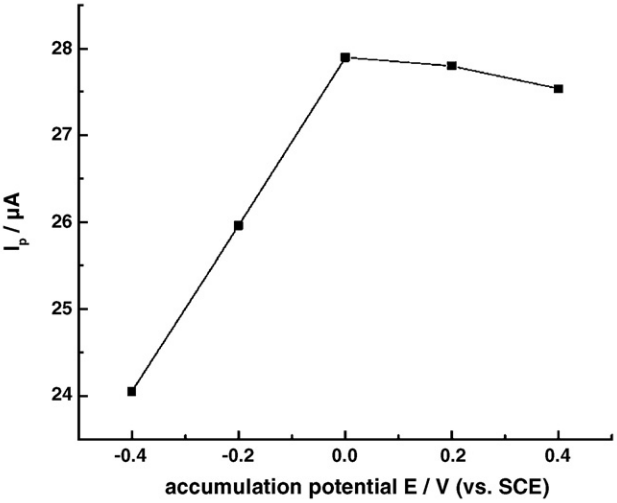

Fig. 6. Influences of accumulation potential on the peak current of 5.0×10^{-5} mol/L diclofenac sodium at MWNTs–DHP film-coated GCE in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0).

MWNTs–DHP film coated GCE in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) and to determine the diffusion coefficient D and Q_{ads} according to the formula given by Anson [27].

$$Q = 2nFAcD^{1/2}\pi^{-1/2}t^{1/2} + Q_{dl} + Q_{ads}.$$

The results are depicted in Fig. 7. Where A is the surface area of the working electrode, C is the concentration of diclofenac sodium, D is the diffusion coefficient of diclofenac sodium, Q_{ads} is the adsorption charge. Other symbols have their usual significances. In this work, $A=0.072$ cm^2, determined in 5 mM $K_4Fe(CN)_6$ and 0.1 M KCl solution, $c=4\times10^{-4}$ mol/L, and slope is 7.4742 μC/s$^{1/2}$. The same values of double-layer charge Q_{dl} could be obtained in the absence and presence of diclofenac sodium at the same electrode. So after the subtraction of the background charge obtained in the absence of diclofenac sodium, which can eliminate the effect of double-layer charge Q_{dl} in this experiment, the plots of Q against t in Fig. 7 are converted into the plots of Q against $t^{1/2}$. It is clear that the charges (Q) have linear relationships with the square roots of time ($t^{1/2}$) for the oxidation reaction (inset in Fig. 7). According to the integrated Cottrell equation, the number of electron involved in the oxidation of diclofenac sodium can be estimated from the slope of the plot of Q vs. $t^{1/2}$. On the assumption that the value of n is 1, it is calculated that the diffusion coefficient of diclofenac sodium in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) is 5.68×10^{-6} cm^2/s. Q_{ads} can be obtained by the difference of the intercepts of the plot of Q vs. $t^{1/2}$ in the presence and absence of diclofenac sodium. Here Q_{ads} is 24.7832 μC, according the equation $Q_{ads}=nFA$, the value of Γ is 3.57×10^{-9} mol/cm^2.

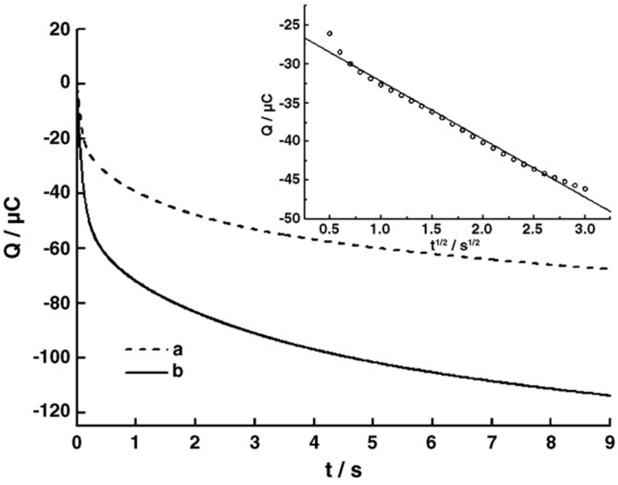

Fig. 7. Chronocoulometry of 4.0×10^{-4} mol/L diclofenac sodium at MWNTs–DHP film coated GCE in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) (curve b). Curve a stands for that in the blank solution. The inset shows the linear relationship between the charges (Q) and the square roots of times ($t^{1/2}$) for the oxidation reaction (background subtracted). Initial potential 0.55 V, final potential 0.80 V, and pulse width 9 s.

3.5. Mechanism for the oxidation of diclofenac sodium at MWNTs–DHP composite film

The influences of solution pH on oxidation of diclofenac sodium were investigated by linear sweep voltammetry as shown in Fig. 8. In the range of pH from 2.1 to 7.0, the oxidation peak potential negatively shifts with the increasing of solution pH and obeys the equation:

$$E_p = 0.9086 - 0.0453\mathrm{pH} (R = 0.9999).$$

The slope of 45.3 mV/pH was close to the theoretic value 59 mV/pH, suggesting one electron and one proton transferred in the oxidation of diclofenac sodium. This value of the slope is smaller than 59 mV/pH, perhaps because of the influence of the protonation states of diclofenac sodium or the protonation of the water molecule coordinated to the target molecules.

The effects of scan rate (υ) on the oxidation current of diclofenac sodium were also examined. The peak current increased linearly with the increase of square root of scan rate that

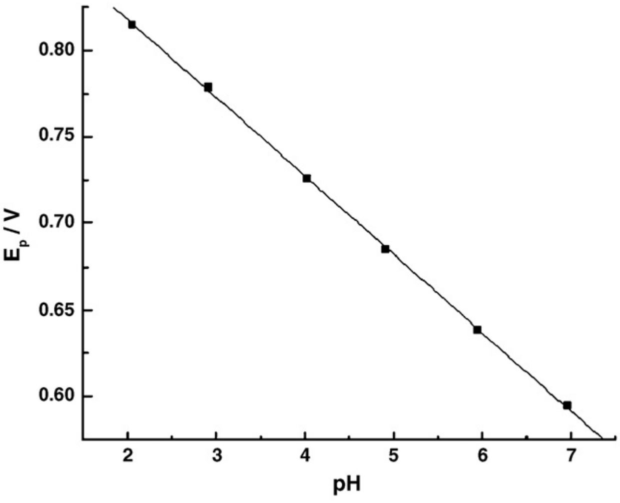

Fig. 8. Effects of solution pH on the peak potential of 5.0×10^{-5} mol/L diclofenac sodium at MWNTs–DHP film-coated GCE in 0.1 mol/L phosphate buffer solution.

ranged from 0.025 to 0.30 V/s, and it can be expressed as follows:

$$I_{\mathrm{p}}(\mu\mathrm{A}) = 195.52\upsilon^{1/2} - 23.83(R = 0.9971)$$

This result shows that the electrode process is controlled by the diffusion step. With increase of scan rate, the relationship between the oxidation peak potential and scan rate is described by the following equation:

$$E_{\mathrm{p}} = 0.03330 \ln \upsilon + 0.7939(R = 0.9920)$$

The results are described in Fig. 9. The slope indicates that the value of αn_{α} is 0.40, where α is the transfer coefficient and n_{α} is the number of the electron transfer in the rate-determining step. On the base of above results, the n_{α} is 1 then the value of α is calculated to be 0.4, which is reasonable for the most of irreversible electrode processes.

Based on above discussions the oxidation process of diclofenac sodium is controlled by the diffusion step and one electron and one proton are involved in the reaction.

3.6. Analysis applications

3.6.1. Calibration and interferences

The calibration curve for diclofenac sodium in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) at MWNTs–DHP coated GCE was established by LSV. The relationship between diclofenac sodium concentration and the oxidation peak current can be described with the following linear regression equations in the range of concentration from 1.7×10^{-7} to 2.5×10^{-6} mol/L and from 2.5×10^{-6} to 7.5×10^{-5} mol/L, respectively:

$$I_{\mathrm{p}}(\mu\mathrm{A}) = 0.09590 + 6.228c(\mu\mathrm{M})\ R = 0.9996$$

$$I_{\mathrm{p}}(\mu\mathrm{A}) = 19.21 + 1.000c(\mu\mathrm{M})\ R = 0.9980.$$

Under the optimized experiment conditions described above, a detection limit of 8.0×10^{-8} mol/L diclofenac sodium was obtained with an accumulation for 4 min at open circuit. The relative standard deviation (RSD) of 2.96% for 10 times parallel detection of 1.0×10^{-5} mol/L diclofenac sodium, and 2.10% for 10 times detection at different electrodes were obtained, suggesting excellent reproducibility and repeatability of MWNTs–DHP modified GCE. Moreover, the stability of this modified electrode was tested in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0) containing 1.0×10^{-5} mol/L diclofenac sodium. The electrode response maintained at a level of about 94.4% of the original after 20 days. This MWNTs–DHP film on GC electrode by simple cast could maintain its original condition without any desquamation phenomenon, suggesting a firm attachment of MWNTs–DHP film to glassy carbon electrode surface.

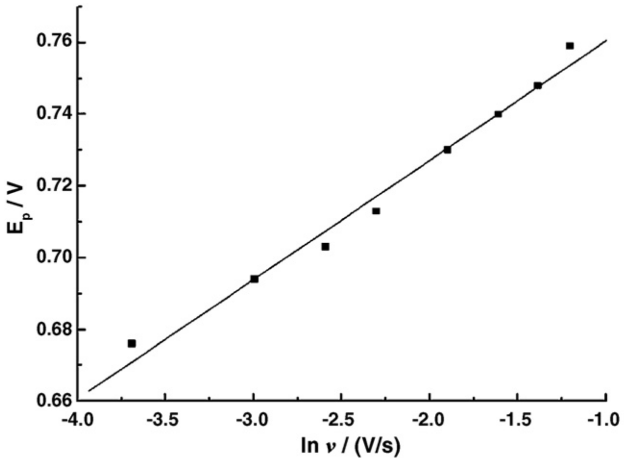

Fig. 9. Effects of scan rate on the peak potential of 5.0×10^{-5} mol/L diclofenac sodium at MWNTs–DHP film-coated GCE in 0.1 mol/L sodium acetate–acetic acid buffer solution (pH 5.0).

Table 3
Determination of diclofenac sodium in diclofenac sodium enteric-coated tablets ($n=5$)

Sample no.	Declared (mg/tablet)	Detected by UV (mg/tablet)	Detected by this method (mg/tablet)	Recovery (%)
1	25	25.24	25.10	100.6
2	25	25.12	24.86	99.5
3	25	24.92	25.08	100.9
4	25	24.90	24.81	102.0
5	25	25.08	25.25	99.3

3.6.2. Determination of diclofenac sodium in diclofenac sodium enteric-coated tablets

The proposed method was applied to the determination of diclofenac sodium in diclofenac sodium enteric-coated tablets. The results are illustrated in Table 3. In this experiment, the concentration of diclofenac sodium was calculated using standard additions method. The relative standard deviation (RSD) of each sample for 5 times parallel detection is less than 4.5%. In addition, the recovered ratio on the basis of this method was investigated and the value is between 99.3% and 102.0%. The recovered ratio indicates that the determination of diclofenac sodium using MWNTs–DHP film-coated GCE is effective and sensitive. At last, in order to estimate the feasibility, precision and efficiency of this method ultraviolet (UV)–visible absorption spectroscopy was recorded to determine diclofenac sodium. The obtained results were compared with those by MWNTs–DHP film-coated GCE (Table 3). The consistence of the results showed that it is feasible and effective.

4. Conclusion

MWNTs have large specific surface area and strong adsorptive properties providing more reaction sites. MWNTs–DHP film on the electrode surface is uniform and porous. Because of these characteristics the adsorption of diclofenac sodium to the electrode surface becomes easy. Correspondingly the concentration of diclofenac sodium at the electrode surface was enlarged. So the oxidation peak current of diclofenac sodium was greatly enhanced at MWNTs–DHP film modified electrode. The electrode process was diffusion-controlled and totally irreversible following a step mechanism involving the total loss of one electron and one proton. Thus the sensitivity for determination of diclofenac sodium increased markedly. The proposed method could be applied to the determination of diclofenac sodium in diclofenac sodium enteric-coated tablets. The results proved that it is feasible and effective.

Acknowledgments

This research is supported by the National Natural Science Foundation of China (Nos. 30370397 and 60571042).

References

[1] Q. Zhao, Z. Gan, Q. Zhuang, Electroanalysis 14 (2002) 1609.

[2] M. Musameh, J. Wang, A. Merkoci, Y. Lin, Electrochem. Commun. 4 (2002) 743.

[3] J.J. Gooding, R. Wibowo, J.Q. Liu, W. Yang, D. Losic, S. Orbons, F.J. Mearns, J.G. Shapter, D.B. Hibbert, J. Am. Chem. Soc. 125 (2003) 9006.

[4] X. Yu, D. Chattopadhyay, I. Galeska, F. Papadimitrakopoulos, J.F. Rusling, Electrochem. Commun. 5 (2003) 408.

[5] J. Wang, A. Kawde, M. Mustafa, Analyst 128 (2003) 912.

[6] P.J. Britto, K.S.V. Santhanam, P.M. Ajayan, Bioelectrochem. Bioenerg. 41 (1996) 121.

[7] J. Wang, M. Li, Z. Shi, N. Li, Z. Gu, Anal. Chem. 74 (2002) 1993.

[8] M. Musameh, J. Wang, A. Merkai, Y. Lin, Electrochem. Commun. 14 (2002) 743.

[9] F.H. Wu, G.C. Zhao, X.W. Wei, Electrochem. Commun. 4 (2002) 690.

[10] P.J. Britto, K.S.V. Santhanam, Adv. Mater. 11 (1999) 154.

[11] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Science 287 (2000) 1801.

[12] W. Huang, S. Taylor, K. Fu, Y. Lin, D. Zhang, T.W. Hanks, A.M. Rao, Y.P. Sun, Nano Lett. 2 (2002) 311.

[13] J.J. Daris, R.J. Coles, H. Allen, D. Hill, J. Electroanal. Chem. 440 (1997) 279.

[14] T. Iliescu, M. Baia, V. Miclăuş, Eur. J. Pharm. Sci. 22 (2004) 487.

[15] N. Gostick, I.G. James, T.K. Khong, P. Roy, P.R. Shepherd, A.J. Miller, Curr. Med. Res. Opin. 12 (1990) 135.

[16] B. Crowley, J.J. Hamill, S. Lyndon, J.F. Mckellican, P. Williams, A.J. Miller, Curr. Med. Res. Opin. 12 (1990) 143.

[17] W. Jin, J. Zhang, J. Chromatogr., A 868 (2000) 101.

[18] L. González, G. Yuln, M.G. Volonté, J. Pharm. Biomed. Anal. 20 (1999) 487.

[19] M.E. Abdel-Hamid, L. Novotny, H. Hamza, J. Pharm. Biomed. Anal. 24 (2001) 587.

[20] J.C. Botello, G. Pérez-Caballero, Talanta 42 (1995) 105.

[21] L.A. Carreira, M. Rizk, Y. EI-Shabrawy, N.A. Zakhari, S.S. Toubar, J. Pharm. Biomed. Anal. 13 (1995) 1331.

[22] S.W. Sun, H. Fabre, J. Liq. Chromatogr. 17 (1994) 433.

[23] S.W. Sun, H. Maillols, J. Liq. Chromatogr. 17 (1994) 2495.

[24] A. Siou, F. Pommier, J. Godbillon, J. Chromatogr. 571 (1991) 87.

[25] D. Lansdorp, T.J. Janssen, P.J.M. Gurlen, T.B. Vree, J. Chromatogr. 528 (1990) 487.

[26] M.T. Xu, L.F. Chen, J.F. Song, Anal. Biochem. 329 (2004) 21.

[27] F.C. Anson, Anal. Chem. 36 (1964) 932.